Surface Partition of Large Clusters

K. A. Bugaev[1,2], L. Phair[1] and J. B. Elliott[1]

[1] *Nuclear Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720*

[2] *Bogolyubov Institute for Theoretical Physics, Kiev, Ukraine*

During last forty years the Fisher droplet model (FDM) [1] has been successfully used to analyze the condensation of a gaseous phase (droplets or clusters of all sizes) into a liquid. The systems analyzed with the FDM are many and varied, but up to now the source of the surface entropy is not absolutely clear. In his original work Fisher postulated that the surface free-energy F_A of a cluster of A-constituents consists of surface ($A^{2/3}$) and logarithmic ($\ln A$) parts, i.e. $F_A = \sigma(T)\ A^{2/3} + \tau T \ln A$. Its surface part $\sigma(T)\ A^{2/3} \equiv \sigma_{\rm o}[1\ -\ T/T_c]\ A^{2/3}$ consists of the surface energy, i.e. $\sigma_{\rm o}\ A^{2/3}$, and surface entropy $-\sigma_{\rm o}/T_c\ A^{2/3}$. From the study of the combinatorics of lattice gas clusters in two dimensions, Fisher postulated the specific temperature dependence of the surface tension $\sigma(T)|_{\rm FDM}$ which gives naturally an estimate for the critical temperature T_c. Surprisingly Fisher's estimate works for the 3-d Ising model, nucleation of real fluids and nuclear multifragmentation.

To understand why the surface entropy has such a form we formulated a statistical model of surface deformations of the cluster of A-constituents, the Hills and Dales Model (HDM) [2]. For simplicity we consider cylindrical deformations of positive height $h_k > 0$ (hills) and negative height $-h_k$ (dales), with k-constituents at the base. It is assumed that cylindrical deformations of positive height $h_k > 0$ (hills) and negative height $-h_k$ (dales), with k-constituents at the base, and the top (bottom) of the hill (dale) has the same shape as the surface of the original cluster of A-constituents. We also assume that: (i) the statistical weight of deformations $\exp\left(-\sigma_{\rm o}|\Delta S_k|/s_1/T\right)$ is given by the Boltzmann factor due to the change of the surface $|\Delta S_k|$ in units of the surface per constituent s_1; (ii) all hills of heights $h_k \le H_k$ (H_k is the maximal height of a hill with a base of k-constituents) have the same probability dh_k/H_k besides the statistical one; (iii) assumptions (i) and (ii) are valid for the dales.

The HDM grand canonical surface partition (GCSP)

$$Z(S_A) = \sum_{\{n_k^\pm=0\}}^{\infty} \left[\prod_{k=1}^{K_{max}} \frac{\left[z_k^+ \mathcal{G}\right]^{n_k^+}}{n_k^+!} \frac{\left[z_k^- \mathcal{G}\right]^{n_k^-}}{n_k^-!} \right] \Theta(s_1 \mathcal{G}) \quad (1)$$

corresponds to the conserved (on average) volume of the cluster because the probabilities of hill z_k^+ and dale z_k^- of the same k-constituent base are identical [2]

$$z_k^\pm \equiv \int\limits_0^{\pm H_k} \frac{dh_k}{\pm H_k}\, e^{-\frac{\sigma_{\rm o} P_k |h_k|}{T s_1}} = \frac{T s_1}{\sigma_{\rm o} P_k H_k} \left[1 - e^{-\frac{\sigma_{\rm o} P_k H_k}{T s_1}} \right]. \quad (2)$$

Here P_k is the perimeter of the cylinder base.

The geometrical partition (degeneracy factor) of the HDM or the number of ways to place the center of a given deformation on the surface of the A-constituent cluster which is occupied by the set of $\{n_l^\pm = 0, 1, 2, ...\}$ deformations of the l-constituent base we assume to be

$$\mathcal{G} = \left[S_A - \sum_{k=1}^{K_{max}} k\,(n_k^+\ +\ n_k^-)\, s_1 \right] s_1^{-1}\,, \quad (3)$$

where $s_1 k$ is the area occupied by the deformation of k-constituent base ($k = 1, 2, ...$), S_A is the full surface of the cluster, and $K_{max}(S_A)$ is the A-dependent size of the maximal allowed base on the cluster.

The $\Theta(s_1\mathcal{G})$-function in (1) ensures that only configurations with positive value of the free surface of cluster are taken into account, but makes the analytical evaluation of the GCSP (1) very difficult. However, we were able *to solve this GCSP exactly* for any surface dependence of $K_{max}(S_A)$ using the Laplace-Fourier transform technique [3]:

$$Z(S_A)\ = \sum_{\{\lambda_n\}} e^{\lambda_n\, S_A} \left[1 - \tfrac{\partial \mathcal{F}(S_A, \lambda_n)}{\partial \lambda_n} \right]^{-1}. \quad (4)$$

The poles λ_n of the isochoric partition are defined by

$$\lambda_n\ =\ \mathcal{F}(S_A, \lambda_n) \equiv \sum_{k=1}^{K_{max}(S_A)} \left[\frac{z_k^+}{s_1} + \frac{z_k^-}{s_1} \right]\ e^{-k\, s_1 \lambda_n}\,. \quad (5)$$

Our analysis shows that Eq. (5) has exactly one real root $R_0 = \lambda_0, Im(\lambda_0) = 0$, which is the rightmost singularity, i.e. $R_0 > Re(\lambda_{n>0})$. As proved in [2], the real root R_0 dominates completely for clusters with $A \ge 10$.

Also we showed that there is an absolute supremum for the real root R_0, which corresponds to the limit of infinitesimally small amplitudes of deformations, $H_k \to 0$, of large clusters: $\sup(R_0)\ =\ 1.06009\ \equiv\ R_0\ = 2\left[e^{R_0} - 1\right]^{-1}$. It is remarkable that the last result is, first, model independent because in the limit of vanishing amplitude of deformations all model specific parameters vanish; and, second, it is valid for any self-non-intersecting surfaces.

For large spherical clusters the GCSP becomes $Z(S_A)\ \approx\ 0.3814\ e^{1.06009\, A^{2/3}}$, which, combined with the Boltzmann factor of the surface energy $e^{-\sigma_{\rm o} A^{2/3}/T}$, generates the following temperature dependent surface tension of the large cluster $\sigma(T) = \sigma_{\rm o}\left[1 - 1.06009 \frac{T}{\sigma_{\rm o}}\right]$. This result means that the actual critical temperature of the FDM should be $T_c = \sigma_{\rm o}/1.06009$, i.e. 6.009 % smaller in $\sigma_{\rm o}$ units than Fisher originally supposed.

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[1] M. E. Fisher, Physics **3** (1967) 255.
[2] K. A. Bugaev, L. Phair and J. B. Elliott, nucl-th/0406034.
[3] K. A. Bugaev, arXiv:nucl-th/0406033.